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**Title of the Invention: Method for Manufacturing Liquid Crystal
Polymer Film or Sheet**

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(54) Title of the Invention: Method for Manufacturing Liquid Crystal Polymer Film or Sheet

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(72) Inventor: Eiji Yamamoto (c/o Central Research Laboratories, Unitika, Ltd.,
23-banchi, Uji Kozakura, Uji-shi, Kyoto-fu)

(72) Inventor: Minoru Kishida (same address as above)

(71) Applicant: Unitika, Ltd.
1-50 Higashi-Motomachi, Amagasaki-shi, Hyogo-ken

SPECIFICATION

1. Title of the Invention

Method for Manufacturing Liquid Crystal Polymer Film or Sheet

2. Claims

(1) A method for manufacturing a liquid crystal polymer film or sheet, characterized in that a film or sheet consisting of a thermotropic liquid crystal polymer containing p-hydroxybenzoic acid, terephthalic acid and ethylene glycol as the main components is subjected to a roll calender treatment (A) within a temperature range in which the temperature of the film or sheet is at least the glass transition temperature and at most the melting temperature, and (B) within a range in which the linear pressure of the roll calender is at least 100 kg/cm and at most 3000 kg/cm.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a manufacturing method suitable for producing a liquid crystal film or sheet that shows little irregularity in thickness.

(Prior Art and Problems to Be Solved by the Invention)

As is universally known, most polyesters that can form anisotropic melts, i.e., so-called thermotropic liquid crystal polyesters, can be molded in the molten state and have properties such as a high heat resistance, high dimensional stability, high strength, high elastic modulus, high gas barrier properties and the like. Accordingly, the use of such polyesters in fibers, films, injection-molded articles and the like has attracted attention, and some applications have already been adapted for practical use. However, the conspicuous uniaxial orientation, which is a characterizing feature of liquid crystal polymers (polyesters), is a problem, so that it is generally difficult to obtain biaxially oriented films or sheets, and extremely difficulty is encountered in the case of manufacturing methods in which a T die is used. However, if a method is used in which stress is applied not only in the longitudinal direction (MD) but also in the lateral direction (TD) (such as an inflation method), films or sheets that are biaxially oriented in the longitudinal and lateral directions can be obtained. On the other hand, in the case of manufacture by an inflation method, there are limits to gap adjustment of the lip due to the die structure, so that irregularity in the thickness of the film or sheet is much worse than in a T die method.

An object of the present invention is to manufacture a superior liquid crystal polymer film that is free from such problems.

(Means Used to Solve the Above-Mentioned Problems)

The present inventors conducted diligent research concerning the abovementioned problems. As a result of this research, the inventors perfected the present invention, the main point of which is a method for manufacturing a liquid crystal polymer film or sheet characterized in that a film or sheet consisting of a thermotropic liquid crystal polymer containing p-hydroxybenzoic acid, terephthalic acid and ethylene glycol as the main components is subjected to a roll calender treatment (A) within a temperature range in which the temperature of the film or sheet is at least the glass transition temperature and at most the melting temperature, and (B) within a

range in which the linear pressure of the roll calender is at least 100 kg/cm and at most 3000 kg/cm.

If it is attempted to perform a roll calender treatment at a temperature exceeding the melting point, the film undergoes thermal degradation or the film fuses to the rolls, so that a treatment cannot be performed. Furthermore, the linear pressure of the roll calender is determined in accordance with the roll calender treatment temperature. However, at a linear pressure that is less than 100 kg/cm, the problem of irregular thickness cannot be sufficiently solved. On the other hand, if the linear pressure is set at a value exceeding 3000 kg/cm, it becomes difficult to control the film or sheet to the target thickness, and there may be cases in which the balance of performance values suffers.

In the roll calender method of the present invention, it is possible to eliminate all of the abovementioned problems by using a high pressure without melting the polymer. Specifically, the inventors discovered that this method is effective as a method that reduces the irregularity in the thickness while substantially maintaining the physical properties, molecular orientation and the like of the liquid crystal polymer film or sheet, and that this achievement leads to an extremely superior commercial effect.

In the present invention, the term "thermotropic liquid crystal polyester" refers to a polyester that has the property of forming an optically anisotropic melt. This is a polyester which has the property of allowing the passage of polarized light in a molten state in an optical system equipped with polarizers that cross each other at 90°. Typical examples of such polyesters include (1) polyesters consisting chiefly of p-hydroxybenzoic acid, (2) polyesters consisting chiefly of 2-hydroxy-6-carboxynaphthalene, (3) polyesters consisting chiefly of terephthalic acid and hydroquinones, (4) polyesters consisting of a p-hydroxybenzoic acid component and a polyethylene terephthalate component, or the like. Within limits that cause no loss of the physical properties of the liquid crystal polyester, such polymers may also appropriately contain aromatic components such as isophthalic acid, m-hydroxybenzoic acid, 4,4'-dicarboxy biphenyl, 2,6-naphthalenedicarboxylic acid, 4,4'-dicarboxy diphenyl ether, resorcin, hydroquinone, 2,6-dihydroxynaphthalene, 4,4'-dihydroxybiphenyl, 2-phenylhydroquinone, 2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl)sulfone, 2,2-bis(4-β-hydroxy-

ethoxyphenyl)propane, bis(4- β -hydroxyethoxyphenyl)sulfone and the like; aliphatic components such as malonic acid, succinic acid, suberic acid, adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, tetradecanedioic acid, eicosanedioic acid, trimethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, polyethylene glycols and the like; and alicyclic components such as 1,4-cyclohexanedicarboxylic acid, 1,4-cyclohexanedimethanol and the like, as copolymerized components. Furthermore, such polymers may also contain additives such as flame retarding agents, heat-resistant agents, light-resistant agents, delustering agents, pigments and the like.

Especially desirable among the abovementioned polyesters are polyesters of type (4), and a polyester consisting of a p-hydroxybenzoic acid component in a ratio of 30 to 74 mol%, a polyethylene terephthalate component in a ratio of 35 to 74 mol% and ethylene glycol in a ratio of 13 to 35 mol% is [especially] suitable from the standpoint of superior molten moldability and workability. For example, this liquid crystal polyester can be manufactured by a method in which a polyethylene terephthalate and p-acetoxybenzoic acid are mixed, an acidolysis reaction is then performed by heating and melting this mixture, and polycondensation is performed under reduced pressure.

Next, an inflation method is effective as a method for manufacturing a film consisting of a thermotropic liquid crystal polyester according to the present invention. For this purpose, an arbitrary polymer consisting of a thermotropic liquid crystal polyester can be selected. In this case, it is desirable from a practical standpoint that the respective degrees of orientation in the longitudinal direction (MD) and the direction (TD) that is perpendicular to this longitudinally direction be balanced. In a case where the characteristic is expressed as tensile strength, it is desirable that the ratio between MD and TD be 5:1 to 1:3, preferably 4:1 to 1:2.

A steel/steel roll calender is desirable for the roll calender treatment of the molded article; however, but steel/rubber rolls and/or rubber/rubber rolls may also be used. Furthermore, in regard to the roll pressing method, any desired method such as a spring system or mechanical system, as well as an oil pressure system, air system, electromagnetic system, water pressure system or the like may be used. A large pressing force is desirable. Roll heating methods that can be used include catalytic heating, induction heating and the like. It is important that the roll

temperature be set in accordance with the pressing force, and any desired heating method may be used.

(Working Examples)

Next, the present invention will be described more concretely in terms of working examples.

Working Example 1 and Comparative Examples 1 Through 3

Polyester chips with an intrinsic viscosity of 0.71 and powdered p-acetoxybenzoic acid were placed in a reactor at a molar ratio of 20/80, and after the raw materials were sufficiently dried, the temperature was elevated to 280°C while a very small amount of nitrogen gas was caused to flow through the reaction system. After all of the raw materials were melted, the system was maintained at this temperature for 40 minutes, so that acetic acid was caused to flow out, thus performing an acidolysis reaction. Afterward, pressure reduction was initiated using a pressure reduction schedule that resulted in a full vacuum (1 torr) being achieved in 90 minutes, and after a polycondensation reaction was performed in a molten phase, the product was converted into chips by an ordinary method. The melting point of the polyester resin thus obtained was 280°C, the crystallization temperature (during cooling) was 220°C and the glass transition temperature was 79°C. Liquid crystal properties were exhibited in a molten state, and the intrinsic viscosity was 0.72. A biaxially oriented film with a thickness of 50 μ , obtained by forming this polymer into a film by the inflation method, was subjected to the following experiments.

The method used to determine the melting point in the present invention employed a differential heat scanning calorimeter (manufactured by Perkin Elmer), and approximately 15 mg of sample was measured at a temperature elevation/temperature drop rate of 20°C/[min]. The glass transition temperature was measured at a temperature elevation rate of 2°C/min using a viscoelasticity measuring device Rheovibron.

(1) Roll Calender Treatment

Films were treated at linear pressures of 150, 300 and 3500 kg/cm, roll temperatures of 50, 160 and 290°C and a roll circumferential speed of 3 m/min using a MagnaPower roll calender (manufactured by Bellmatic).

(2) Evaluation of Irregularity in Thickness

A film with a width of 30 cm was measured at 1-cm intervals using a MICROFINE thickness gauge (manufactured by Union Tool), and the result was expressed as the mean value and deviation.

(3) Evaluation of Variation in Mechanical Properties of the Film

The tensile strength values of each film before and after the roll calender treatment were compared.

The experimental results are summarized in Table 1. It can be seen from this table that the roll calender treatment is extremely effective in reducing the irregularity in thickness while causing almost no deterioration in mechanical properties.

Table 1

| | Drawing conditions | | Film performance prior to drawing | | Film performance after drawing | |
|-----------------------|--------------------|---------------|-----------------------------------|-------------------------------------|---------------------------------|-------------------------------------|
| | Temp. | Pressure | Thickness irregularity | Strength | Thickness irregularity | Strength |
| Comparative Example 1 | 160°C | 50 kg/cm | 58 (+13, -13) | (MD/TD) 26/20 kg/cm ² | 52.8 (+ 13, -13) | (MD/TD) 26/21 kg/cm ² |
| Comparative Example 2 | 290°C | 1 kg/cm | " | " | Deterioration, discoloration | Deterioration, discoloration |
| Working Example 1 | 160°C | 300 kg/cm | " | " | 49.0 (+5, -4) | (MD/TD) 25/19 kg/cm ² |
| Comparative Example 3 | 50°C | 3500 kg/cm | " | " | 31.4 (+3, -3) | (MD/TD) 30/9 kg/cm ² |

(Effect of the Invention)

The method of the present invention has an effect in alleviating the thickness irregularity that is a drawback of liquid crystal polymer films manufactured by inflation, and can easily be worked on an industrial scale, so that the value of this method is extremely high.

Applicant: Unitika, Ltd.